Electrocatalytic properties of Co nanoconical structured electrode produced by one-step and two-step method.

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Introduction

One-dimensional (1D) nanostructures, such as nanotubes, nanopores, nanodots and nanocones, are characterised by better catalytic properties than bulk material due to their large active surface area and small geometrical size. There are several methods of synthesis these structures, including the the one- and two-step methods. In the one-step method, a crystal modifier are added to the solution in order to limit horizontal direction of structures growing during electrodeposition. This method allows to fabricate nanocones without using chromic acid, which is dangerous for the environment. In this work, cobalt nanoconical structures were obtained from an electrolyte containing $CoCl_2$, H_3BO_3 and NH_4Cl as the crystal modifier. Another way of production of 1D nanocones is electrodeposition of metal into porous anodic alumina oxide (AAO) templates. This method is called the two-step method. It allows to control the geometrical features of nanostructures due to the features of used template. In this case, AAO template was obtained using two-step anodization. Then, electrodeposition of cobalt was performed from an electrolyte containing $CoSO_4$ and H_3BO_3. To obtain free standing nanocones the template has to be removed by immersion into dilute NaOH solution. The bulk sample was electrodeposited from the same electrolyte.

For determination of catalytic activity of synthesized material hydrogen evolution process have been chosen. The electrocatalytic properties of materials fabricated in one-step and two-step method were measured in 1M NaOH and compared with bulk materials. The microscopic pictures of material before and after hydrogen evolution will be searched and compared in order to detect any degradation of material surface morphology.

Experimental details and results

One-step method:

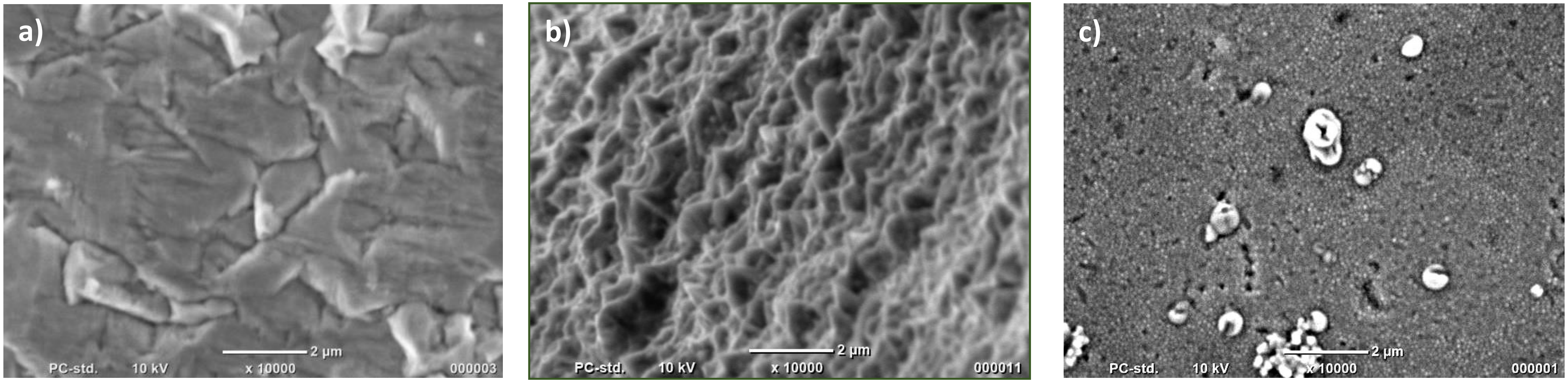
1. Electrochemical polishing of copper substrate,
2. Electrodeposition of Co nanocones.

Two-step method:

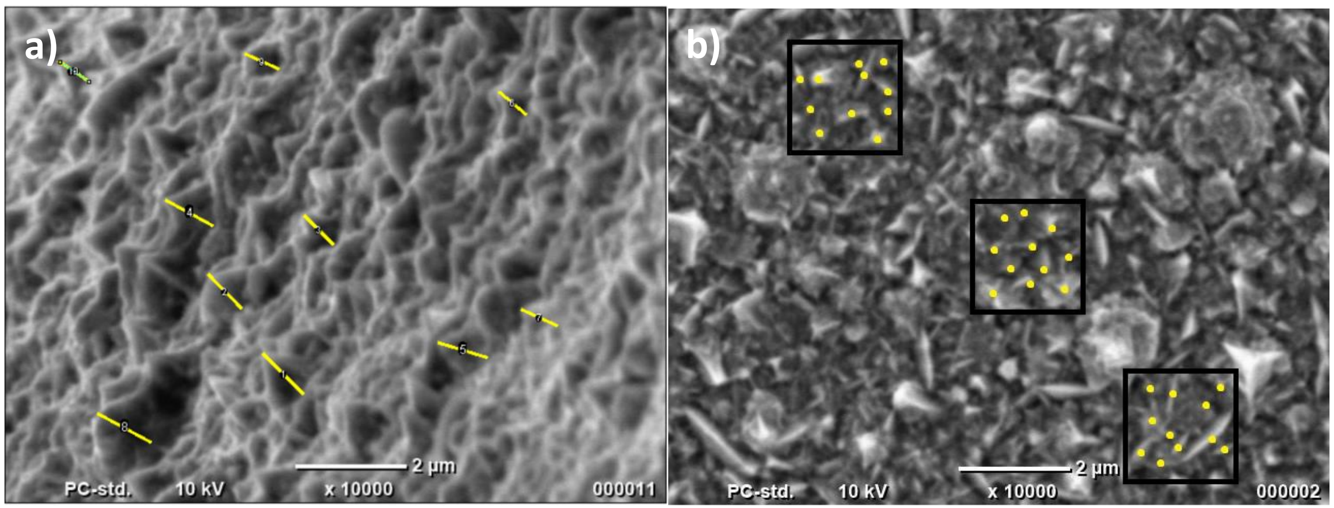
1. Long-period anodization in $H_2C_2O_4$,
2. Removing the formed oxide layer in mixed solution of H_3PO_4 and H_2CrO_4,
3. Alternating cycles of short-anodization in $H_2C_2O_4$ and pore widening process in H_3PO_4 ,
4. Template with conical nanopores,
5. Electrodeposition of metal,
6. Removing of the template in a dilute NaOH solution,
7. Free-standing Co nanocones.

Conditions of the electrodeposition process	
Electrolyte composition	200 g/l $CoCl_2$, 100 g/l H_3BO_3, NH_4Cl as a crystalline modifier (for one-step method)
Concentration of NH_4Cl [g/l]	100 (for the one-step method)
Current density i [mA/cm^2]	20
Temperature [^oC]	60
Time [min]	20

Experimental details and results



SEM photos of a) bulk material, Co nanocones synthesized using b) one-step method and c) two-step method.

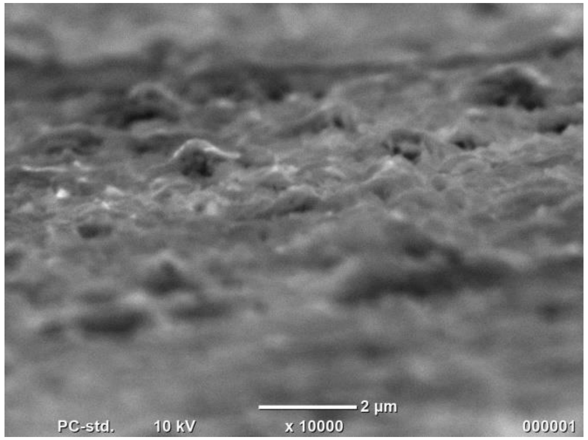


Determination of a) nanocones height and b) number of nanocones using SEM photos.

Material	Height [nm]	Number of nanocones per 1 μm^2	Real acitve surface area [cm^2]
Co nanocones obtained in one-step method	866	2.75	8.05
Co nanocones obtained in two-step method	74	68	3.57
Co bulk	-	-	2.80

Determined real active surface area for all samples.

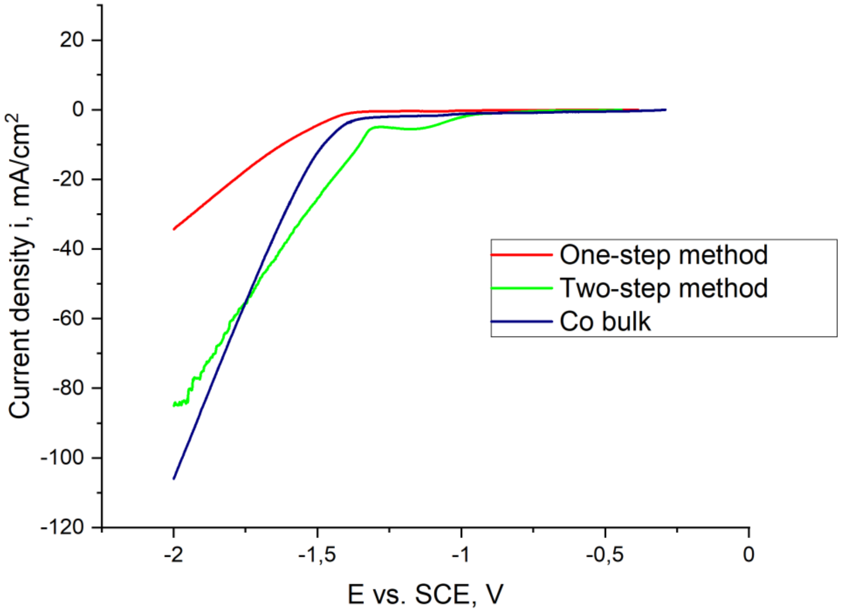
Experimental details and results



Co cones obtained using one-step method after hydrogen evolution reaction.

Material	E_{ONET} [V]
Co nanocones obtained in one-step method	-1.47
Co nanocones obtained in two-step method	-1.29
Co bulk	-1.50

Values of E_{ONSET} for all samples



LSV curves of Co bulk and Co nanocones obtained using one-step and two-step method in 1 M NaOH solution.

Conclusions

1. It is possible to obtain Co nanocones from the electrolytes with the same composition using one-step and two-step method.
2. Synthesized by one-step method Co structures are characterized by greater geometrical size. However, there are several microshells structures.
3. Value of real active surface area was determineted approximately using SEM photos. It is connected with heterogeneous Co cones obtained by one-step method. There was also assumption that their base is round. Inexactness is connected also with quality of Co nanocones produced using two-step method. Their height and diameter were determined earlier using TEM photos.
4. The SEM photo after hydrogen evolution reaction does not show any change on the sample surface. Taking photo of the Co nanocones after this reaction was impossible due to destruction of the layer by the hydrogen bubbles. It can be noticed in the sharp character of the curve.
5. The worst electrocatalytic properties are shown by Co cones obtained by one-step method. It can be connected with assumptions during determinaton of active surface area. However, in this case the hydrogen evolution reaction started earlier than for Co bulk.
6. The hydrogen evolution reaction started the earliest for Co nanocones fabricated by two-step method.

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